

Towards the electron EDM search. Theoretical study of PbF

K.I. Baklanov and A.N. Petrov²

Institute of Physics, Saint Petersburg State University, Saint Petersburg, Petrodvorets 198904, Russia

A.V. Titov and M.G. Kozlov

²*Petersburg Nuclear Physics Institute, Gatchina, Leningrad district 188300, Russia*

We report *ab initio* relativistic correlation calculations of potential curves and spectroscopic constants for four lowest-lying electronic states of the lead monofluoride. We also calculated parameters of the spin-rotational Hamiltonian for the ground $^2\Pi_{1/2}$ and the first excited $A^2\Sigma_{1/2}^+$ states including P, T -odd and P -odd terms. In particular, we have obtained hyperfine constants of the ^{207}Pb nucleus. For the $^2\Pi_{1/2}$ state $A_{\perp} = -6859.6$ MHz, $A_{\parallel} = 9726.9$ MHz and for the $A^2\Sigma_{1/2}^+$ $A_{\perp} = 1720.8$ MHz, $A_{\parallel} = 3073.3$ MHz. Our values of the ground state hyperfine constants are in good agreement with the previous theoretical studies. We discuss and explain seeming disagreement in the sign of the constant A_{\perp} with the recent experimental data. The effective electric field on the electron E_{eff} , which is important for the planned experiment to search for the electric dipole moment of the electron, is found to be 3.3×10^{10} V/cm.

The interest in theoretical study of ^{207}PbF is caused by the planned experiment to search for the simultaneous violation of the time-reversal invariance (T) and space parity (P) [1–4]. The latter may be caused either by the P, T -odd electron-nucleus interaction or by the electric dipole moment of the electron (eEDM, or d_e), which can exist also only due to fundamental P, T -odd interactions [5]. The possible experiments to search for P, T -odd effects in atoms and molecules were discussed in several books and reviews [6–12].

Experiment to search for eEDM with PbF molecule is currently under preparation by the group of Shafer-Ray [3]. PbF molecule has one of the strongest effective electric field E_{eff} on the valence electron, which determines experimentally measured frequency shifts [1, 2]. This experiment can test “new physics” beyond the Standard Model including different supersymmetric models. Many such models predict eEDM in the range between 10^{-28} – 10^{-29} $e \cdot \text{cm}$ (e is the electric charge of the electron), within the reach of the new generation of experiments [12, 13].

Recently McRaven et al. [4] have measured hyperfine structure parameters for the ground and the first excited states of ^{207}PbF and found them to be in disagreement with previous predictions [1, 2]. Taking into account that theoretical studies of the lead monofluoride took place decades ago within rather simple theoretical models we recalculate spectroscopic constants and parameters of the spin-rotational Hamiltonian, H_{sr} for PbF molecule. In particular, we focus on the calculations of the effective electric field on the electron E_{eff} and the hyperfine structure constants for the lead nucleus. Our new results are in reasonable agreement with previous calculations [1, 2]. We discuss the discrepancy between the theory and experiment [4] and argue that it is caused by the incorrect phase factor in the spin-rotational wave function, rather than in the difference in the sign of the hyperfine constant

A_{\perp} .

The Hamiltonian H_{sr} can be written as [2]

$$H_{\text{sr}} = B' \mathbf{J}^2 + \Delta \mathbf{S}' \cdot \mathbf{J} + \mathbf{S}' \mathbf{A} \mathbf{I} + \quad (1)$$

$$+ \mu_0 \mathbf{S}' \mathbf{G} \mathbf{B} - D \mathbf{n} \cdot \mathbf{E} + \quad (2)$$

$$+ W_P \kappa_P \mathbf{n} \times \mathbf{S}' \cdot \mathbf{I} + (W_{P,T} \kappa_{P,T} + W_d d_e) \mathbf{S}' \cdot \mathbf{n}, \quad (3)$$

where the first line corresponds to the rotational structure with Ω -doubling and the hyperfine interaction of the effective electron spin \mathbf{S}' , $S' = \frac{1}{2}$, with the spin of the nucleus \mathbf{I} ; B' is the rotational constant, \mathbf{J} is the electron-rotational angular momentum, Δ is the Ω -doubling constant, \mathbf{A} is the hyperfine structure tensor. The second line describes interaction of the molecule with the external fields \mathbf{B} and \mathbf{E} , \mathbf{n} is the unit vector along the molecular axis, ζ , directed from Pb to F; \mathbf{G} is the G-factor tensor. The last line corresponds to the interaction with the P -forbidden anapole moment of the nucleus, the P, T -odd weak interactions of the electrons with the heavy nucleus and the interaction of eEDM with the internal electric field of the molecule; κ_P and $\kappa_{P,T}$ are the anapole constant and the P, T -odd neutral current constant for Pb nucleus.

Parameters W_i in (3) can not be measured experimentally and have to be found from the molecular electronic structure calculations. Their accurate knowledge is crucial for extracting constants κ_P , $\kappa_{P,T}$, and d_e from the experiment. Expressions for calculating parameters W_i can be found in Refs.[1, 6, 11]. In the literature the effective electric field seen by the unpaired electron is usually used instead of the parameter W_d . It is defined as: $E_{\text{eff}} = W_d |\Omega|$, where $\Omega = \langle \Psi_{\Omega}^e | \mathbf{S}' \cdot \mathbf{n} | \Psi_{\Omega}^e \rangle = \pm 1/2$ and Ψ_{Ω}^e is the electronic wavefunction for the $^2\Pi_{1/2}$ or $^2\Sigma_{1/2}^+$ states.

We used the generalized relativistic effective core potential (GRECP) [14] to simulate the interaction of valence electrons (4 electrons of Pb) with the explicitly ex-

cluded 1s to 4f electrons of Pb (68 core electrons). In addition the 5s, 5p and 5d shells of Pb (treated explicitly with the used GRECP) were frozen. All the electrons of fluorine were treated explicitly. The resulting configurations were: $6s^2 6p^2$ for Pb and $1s^2 2s^2 2p^5$ for F. For Pb we used generalized correlation atomic basis set [15, 16] ($15s16p12d9f$)/[$5s7p4d2f$] and GRECP from the paper [16]. For F we used the ANO-I ($14s9p4d3f$)/[$4s3p2d1f$] atomic basis from the MOLCAS 4.1 library [17].

By means of the complete active space self-consistent field method the molecular orbitals were received. Molecular symmetry was treated by using the C_{2v} point group classification scheme. The next step was to apply the spin-orbit direct configuration interaction (SODCI) approach [18–20] (modified in [21] to account for spin-orbit interaction in configuration selection procedures). The main idea of this method is to use selected singly and doubly excited configurations with respect to some multiconfigurational reference states within the second order perturbation theory. After that the SODCI approach is employed on the space of all the selected configurations.

In the present work we calculated four lowest states, which belonged to the configurations $[\dots]\sigma^2\pi_{1/2}$ (${}^2\Pi_{1/2}$), $[\dots]\sigma^2\pi_{3/2}$ (${}^2\Pi_{3/2}$), $[\dots]\sigma^2\sigma'$ ($A^2\Sigma_{1/2}^+$) and $[\dots]\sigma^2\sigma''$ ($B^2\Sigma_{1/2}^+$). Here σ is mainly formed from the 6s basis function of Pb, $\pi_{1/2}$ and $\pi_{3/2}$ are mainly made from $6p_x$ and $6p_y$ functions of Pb. The orbitals σ' and σ'' are formed from the $6p_z$ and 7s functions of Pb, respectively.

One of the main goals of the present paper was to draw potential curves for the ground and three lowest excited states. Therefore, we made calculations for several internuclear distances (from 3.8 a.u. to 4.2 a.u.) near the ground state equilibrium distance ($R_e = 2.0575 \text{ \AA} \approx 4.0 \text{ a.u.}$).

Equilibrium internuclear distances, vibrational constants, T_e and dipole moments for four lowest states of PbF molecule can be found in Table I (the most precise data, with 0.00005 threshold, are pointed out for the $D(R)$). The PbF properties could be divided into two groups: valence and core ones. The parallel and perpendicular \mathbf{G} -factor components, the electronic dipole molecule moment $D(R)$ or Ω -doubling constant could be related to the valence properties. However, such properties as E_{eff} , A_{\perp} , A_{\parallel} , anapole moment constant W_P or T -odd interaction constant $W_{P,T}$ could be referred to the core ones. Mainly all these properties were calculated for the ground and first excited states at the point 4.0 a.u., which is close to the equilibrium distance. In the core region one should make a four-component relativistic calculation. However, we have performed calculations on two-component orbitals by means of pseudopotential and, therefore, have to apply a restore procedure for four-component orbitals from two-component ones at the next stage. For this purpose the nonvariational one-centre restoration method developed in [14, 22–26]

is employed. One can find the calculated parameters of the spin-rotational Hamiltonian, H_{sr} , in Table III for the ${}^2\Pi_{1/2}$ and $A^2\Sigma_{1/2}^+$ state, respectively (where (a) and (b) of [1] correspond to the minimal and maximal spin-orbital mixing). Finally, in Table II the matrix element values of Ω -doubling constant Δ divided by $2/2MR^2$ ($\Delta/2B'(R)$) and electronic dipole moments are listed for five investigated points and for two electronic states of the molecule.

TABLE I: Internuclear distances, vibrational constants, T_e and dipole moments for four lowest states of PbF molecule

		$R_e(\text{\AA})$	$w_e(\text{cm}^{-1})$	$T_e(\text{cm}^{-1})$	$D(R) (D)$
${}^2\Pi_{1/2}$	[2]	2.06	489		4.62
	Experiment	2.0575	502.7	0	
	This work	2.08	493.6	0	4.26
${}^2\Pi_{3/2}$	Experiment	2.0342	528.7	8263.5	
	This work	2.07	522.3	8258.9	
$A^2\Sigma_{1/2}^+$	[2]	2.18	418		5.5
	Experiment	2.1597	394.7	22556.5	
	This work	2.18	388.5	23380	2.51
$B^2\Sigma_{1/2}^+$	Experiment	1.97	605.7	35644.4	
	This work	1.99	597.8	36583.8	

According to the data pointed out in Table I, T_e values are in good agreement with the experimental data. The obtained equilibrium distance, R_e , have slightly higher value than in the experiment, whereas the presently obtained vibrational constants are in much better agreement with the experiment comparing to those from [2]. Note that the dipole moment $D(R)$ value for the ground state are nearly the same to those obtained in [2], whereas they are decreased approximately two times for the excited state. All data in Table II obtained for $D(R)$ and Ω -doubling constant have been calculated with the 0.0005 threshold. But we should note that we have computed these parameters for point 4.0 a.u. more accurately with 0.00005 threshold. For Ω -doubling these values are -0.361 and 1.46 for the ${}^2\Pi_{1/2}$ and $A^2\Sigma_{1/2}^+$ states, respectively.

Let us thoroughly examine the data obtained in Table III. First of all we would like to discuss the results for the ground state. The first point to note is that the A_{\parallel} value is in the fault bounds, meantime the G_{\parallel} value is increased in two times according to [2]. The effective field constant W_d obtained is the best datum to-date, the anapole moment constant W_P and T -odd interaction constant $W_{P,T}$ increased their values nearly by 50%. The most interesting result concerns the perpendicular hyperfine structure constant A_{\perp} . The sign of the obtained value exactly agree with those in previous works [1, 2]. Since the constants of the H_{sr} such as A_{\perp} , G_{\perp} , Ω -doubling are determined by the off-diagonal matrix element, it is important to fix the phase factors for the wave functions to get the consistent signs of those matrix elements. In our calculations the phase factor is the

TABLE II: Matrix element values of Ω - doubling constant divided to $2B'(R)$ and electronic dipole moments ($1D = 0.3934$ a.u.) for the ground and the second excited states of PbF molecule

H_{sr} constants	$\langle \Psi \Delta / 2B' \Psi \rangle$									
State	$^2\Pi_{1/2}$					$A^2\Sigma_{1/2}^+$				
Internuclear distance	3.8	3.9	4.0	4.1	4.2	3.8	3.9	4.0	4.1	4.2
[2]			-0.347							
[4]			-0.303					1.49		
This work	-0.412	-0.342	-0.369	-0.391	-0.411	1.49	1.42	1.45	1.47	1.49

	D(R) (D)									
State	$^2\Pi_{1/2}$					$A^2\Sigma_{1/2}^+$				
Internuclear distance	3.8	3.9	4.0	4.1	4.2	3.8	3.9	4.0	4.1	4.2
[2]			4.62					5.5		
This work	4.27	4.264	4.28	4.266	4.255	2.32	2.42	2.55	2.67	2.79

same as in eq. (14) of [1].

In the experimental work [4] of the Shafer-Ray group the obtained A_{\perp} values are nearly the same by absolute value but have the opposite sign for both states. However, it was noted in [4] that the energy level structure is determined by the expression, in which A_{\perp} is multiplied by p , where $p = \pm 1$ is the parity of the electronic-rotational state. Therefore, it was suggested that the parity rather than sign of A_{\perp} has been incorrectly assigned in previous works. However, we believe that the changes in parity or sign of the perpendicular component are not necessary. Some corrections for the energy level expression are required instead. As we found, $(-1)^{J+1/2}$ should be replaced by $(-1)^{J-1/2}$ in eqs. (9) and (23) of [1]. This leads to change of sign in front of pA_{\perp} in eq. (24) of [1] for the energy level structure.

Let us consider the symmetry properties of wavefunction of a diatomic molecule at the space inversion operation in more details. Let x, y, z be a laboratory axes, and the ξ, η, ζ body frame axes in which the molecule is fixed. The α and β ($\gamma = 0$) Euler angles are defined in such a way that the ζ axis coincides with the molecule axis. The vibrational wavefunction is not important here, and electronic-rotational wavefunction within the adiabatic approximation in the Hund case c is written as

$$\Psi_{\Omega}^e(\dots, \xi_a, \eta_a, \zeta_a, \tilde{\sigma}_a, \dots, R) \theta_{M_J, \Omega}^J(\alpha, \beta), \quad (4)$$

where M_J is projection of the total angular momentum, J , on the z axis, subscript a enumerate electrons, $\tilde{\sigma}_a = \pm 1$ is the spin variable which corresponds to the projection of the spin of the a -th electron on the ζ axis, R is the internuclear distance. $\theta_{M_J, \Omega}^J(\alpha, \beta) = \sqrt{\frac{2J+1}{4\pi}} D_{M_J, \Omega}^J(\alpha, \beta, \gamma = 0)$ is rotational wavefunction. In the laboratory system of coordinates the inversion operation, \hat{P} , is

$$\begin{aligned} \hat{P} \tilde{\Psi}_{\Omega}^e(\dots, x_a, y_a, z_a, \sigma_a \dots, R, \alpha, \beta) \theta_{M_J, \Omega}^J(\alpha, \beta) = \\ \tilde{\Psi}_{\Omega}^e(\dots, -x_a, -y_a, -z_a, \sigma_a \dots, R, \alpha + \pi, \pi - \beta) \\ \times \theta_{M_J, \Omega}^J(\alpha + \pi, \pi - \beta), \end{aligned}$$

where $\Psi_{\Omega}^e = \hat{U} \tilde{\Psi}_{\Omega}^e$, $\hat{U} = \exp(i\beta J_2^e) \cdot \exp(i\alpha J_3^e)$ is the unitary operator. Then one can obtain that the inversion, $\hat{P} = \hat{U} \hat{P} \hat{U}^+$, in the body frame system of coordinates is

$$\begin{aligned} \hat{P} \Psi_{\Omega}^e(\dots, \xi_a, \eta_a, \zeta_a, \tilde{\sigma}_a, \dots, R) \theta_{M_J, \Omega}^J(\alpha, \beta) = \\ i^N \Psi_{\Omega}^e(\dots, -\xi_a, \eta_a, \zeta_a, -\tilde{\sigma}_a, \dots, R) \\ \times \theta_{M_J, \Omega}^J(\alpha + \pi, \pi - \beta), \quad (5) \end{aligned}$$

where $i = \sqrt{-1}$, N is the number of electrons. Note that the above transformation of the electronic wavefunction (corresponding to the reflection in the $\eta - \zeta$ plane) gives the electronic wavefunction with the opposite sign of Ω , which has the same adiabatic potential. In the case of $\Omega = 0$ electronic wavefunction whether not changed or is multiplied by the -1 factor. The rotational wavefunctions are also transformed into each other with changing sign of Ω [27]:

$$\theta_{M_J, \Omega}^J(\alpha + \pi, \pi - \beta) = (-1)^{J+2\Omega} \theta_{M_J, -\Omega}^J(\alpha, \beta) \quad (6)$$

The total electronic-rotational wavefunction (4), except the case $\Omega = 0$, has no definite parity. In the case $\Omega \neq 0$ two wavefunctions (4) with different signs of Ω are transformed into each other, and we can form from them positive ($p = 1$) and negative ($p = -1$) wavefunctions. Let us construct the electronic-rotational wavefunction with definite parity for the case $\Omega = \pm 1/2$ of our interest, and, in particular, for the $^2\Pi_{1/2}$ and $^2\Sigma^+$ states. Since the closed electronic shell is invariant under reflection, consider transformation only of the valence spinor $\varphi_{\omega}^e(\xi_a, \eta_a, \zeta_a, \tilde{\sigma})$, where $\omega = \pm 1/2$ is projection of the total angular momentum, j , of the valence electron on the ζ axis. One can verify that for phase factors accepted by eq. (14) of [1]

$$i\varphi_{1/2}^e(-\xi_a, \eta_a, \zeta_a, -\tilde{\sigma}) = i\varphi_{-1/2}^e(\xi_a, \eta_a, \zeta_a, \tilde{\sigma}) \quad (7)$$

and hence, accounting for (6) and (7), the electronic-rotational wavefunction $|J, M_J, p\rangle$ with parity p becomes

$$\begin{aligned} |J, M_J, p\rangle = \\ \Psi_{1/2}^e \theta_{M_J, 1/2}^J + (-1)^{J-1/2} p \Psi_{-1/2}^e \theta_{M_J, -1/2}^J \quad (8) \end{aligned}$$

Eq. (23) of [1] is reduced to (8) by replacing $(-1)^{J+1/2}$ on $(-1)^{J-1/2}$.

The parallel hyperfine structure components is in agreement with [4]. The other data for the first excited $A^2\Sigma_{1/2}^+$ state, listed in the Table III, were obtained for the first time.

Finally, we would like to note that we have performed the most accurate to date electronic structure calculation of the lowest states of PbF and, as a result, have obtained the most reliable data for the spin-rotational Hamiltonian constants. In this paper we have proposed solution of the problem of the sign mismatching in the perpendicular hyperfine structure constant. The new computed data for the spectroscopic constants better conform to the experimental results at present. The calculated effective electric field on the electron is increased in the present study nearly by 10% compared to that in [2].

K.B. and A.P. are grateful to the Ministry of Education and Science of Russian Federation (Program for Development of Scientific Potential of High School) for the Grant No. 2.1.1/1136. A. T. and A.P. were supported by the RFBR grant 09-03-01034

-
- [1] M. G. Kozlov, V. I. Fomichev, Yu. Yu. Dmitriev, L. N. Labzovsky, and A. V. Titov, J. Phys. B **20**, 4939 (1987).
 - [2] Yu. Yu. Dmitriev, Yu. G. Khait, M. G. Kozlov, L. N. Labzovsky, A. O. Mitrushenkov, A. V. Shtoff, and A. V. Titov, Phys. Lett. A **167**, 280 (1992).
 - [3] N. E. Shafer-Ray, Phys. Rev. A **73**, 034102 (2006).
 - [4] C. P. McRaven, P. Sivakumar, and N. E. Shafer-Ray, Phys. Rev. A **78**, 054502(R) (2008), erratum: Phys. Rev. A **80**, 029902(E) (2009).
 - [5] L. D. Landau, Sov. Phys.-JETP **5**, 336 (1957).
 - [6] M. Kozlov and L. Labzovsky, J. Phys. B **28**, 1933 (1995).
 - [7] I. B. Khriplovich and S. K. Lamoreaux, *CP Violation without Strangeness. The Electric Dipole Moments of Particles, Atoms, and Molecules* (Springer-Verlag, Berlin, 1997).
 - [8] E. D. Commins, Adv. At. Mol. Opt. Phys. **40**, 1 (1998).
 - [9] J. S. M. Ginges and V. V. Flambaum, Phys. Rep. **397**, 63 (2004).
 - [10] J. Erler and M. J. Ramsey-Musolf, Prog. Part. Nucl. Phys **54**, 351 (2005).
 - [11] A. V. Titov, N. S. Mosyagin, A. N. Petrov, T. A. Isaev, and D. P. DeMille, Progr. Theor. Chem. Phys. **B 15**, 253 (2006).
 - [12] M. Raidal et al., Eur. Phys. J. C **57**, 13 (2008), arXiv: 0801.1826.
 - [13] E. N. Fortson, P. Sandars, and S. Barr, Physics Today **56(6)**, 33 (2003).
 - [14] A. V. Titov and N. S. Mosyagin, Int. J. Quantum Chem. **71**, 359 (1999).
 - [15] N. S. Mosyagin, E. Eliav, A. V. Titov, and U. Kaldor, J. Phys. B **33**, 667 (2000).
 - [16] T. A. Isaev, N. S. Mosyagin, M. G. Kozlov, A. V. Titov, E. Eliav, and U. Kaldor, J. Phys. B **33**, 5139 (2000).
 - [17] K. Andersson, M. R. A. Blomberg, M. P. Fülscher, G. Karlström, R. Lindh, P.-A. Malmqvist, P. Neogrády, J. Olsen, B. O. Roos, A. J. Sadlej, et al. (1999), quantum-chemical program package “MOLCAS”, Version 4.1.
 - [18] R. J. Buenker and S. D. Peyerimhoff, Theor. Chim. Acta **35**, 33 (1974).
 - [19] R. J. Buenker and S. Krebs, in *Recent Advances in Multireference Methods*, edited by K. Hirao (World Scientific, Singapore, 1999), pp. 1–29.
 - [20] A. B. Alekseyev, H.-P. Liebermann, and R. J. Buenker, in *Recent Advances in Relativistic Molecular Theory*, edited by K. Hirao and Y. Ishikawa (World Scientific, Singapore, 2004), pp. 65–105.
 - [21] A. V. Titov, N. S. Mosyagin, A. B. Alekseyev, and R. J. Buenker, Int. J. Quantum Chem. **81**, 409 (2001).
 - [22] A. V. Titov, Ph.D. thesis, St.-Petersburg (Leningrad) State University, Russia (1985).
 - [23] A. V. Titov, Int. J. Quantum Chem. **57**, 453 (1996).
 - [24] A. V. Titov, N. S. Mosyagin, and V. F. Ezhov, Phys. Rev. Lett. **77**, 5346 (1996).
 - [25] A. N. Petrov, N. S. Mosyagin, T. A. Isaev, A. V. Titov, V. F. Ezhov, E. Eliav, and U. Kaldor, Phys. Rev. Lett. **88**, 073001 (2002).
 - [26] A. N. Petrov, A. V. Titov, T. A. Isaev, N. S. Mosyagin, and D. P. DeMille, Phys. Rev. A **72**, 022505 (2005).
 - [27] L. D. Landau and E. M. Lifshitz, *Quantum mechanics* (Pergamon, Oxford, 1977), 3rd ed.
 - [28] E. R. Meyer and J. L. Bohn, Phys. Rev. A **78**, 010502(R) (2008), URL <http://link.aps.org/abstract/PRA/v78/e010502>.

TABLE III: Parameters of the spin-rotational Hamiltonian H_{sr} for $^2\Pi_{1/2}$ and $A^2\Sigma_{1/2}^+$ states of PbF molecule

State	Reference	A_{\perp} (MHz)	A_{\parallel} (MHz)	G_{\perp}	G_{\parallel}	$W_d(10^{25})\text{Hz}/e\text{ cm}$	$W_{P,T}(\text{KHz})$	$W_P(\text{KHz})$
$^2\Pi_{1/2}$	[2]	-8990	10990	-0.326	0.040	1.4	55	-0.72
	[4]	7200 ± 150	10300 ± 800					
	[28]					1.5		
	[1] (a)	-7460	8690	-0.269	0.034	1.0	51	-0.65
	[1] (b)	-8240	9550	-0.438	0.114	1.8	99	-1.25
	This work	-6859.6	9726.9	-0.319	0.082	1.6	74.95	-0.99
$A^2\Sigma_{1/2}^+$	[4]	-1200 ± 300	3000 ± 2500					
	This work	1720.8	3073.3	2.417	1.92	2.5	123.7	-1.588